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Intermediate Species Absorbing in the 500-nm Region in Nonenzymatic Pyridoxal Catalysis.*

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A key step in the action of almost all pyridoxal enzymes is the formation of a quinonoid species, in which the α -carbon in a Schiff base (aldimine) is deprotonated. Several enzymes have been reported to exhibit an intense absorption band in the 500-nm region of the spectrum, which has been ascribed to the quinonoid species. We reported previously that in methanolic solutions pyridoxal and ethyl alaninate with Al(III) gave an intense absorption band at 488 nm, but not with divalent ions under the same conditions [1].

We now report that the 500-nm absorbing species was formed in the following nonenzymatic reactions in methanol. Isomerization between a ketimine from ethyl pyruvate and PM and an aldimine from ethyl alaninate and PL catalyzed by the 1 : 1 Cu(II) chelates of ethylenediamine(en), dipyridyl(dipy) and tripyridyl(tripy). The quinonoid species were stabilized in the ternary complexes such as Cu(II)-quinonoid-en. The fact that a similar ternary complex was not fully formed with diethylenetriamine(dien) should indicate the coplanarity of the quinonoid species.

* 本報告は "Enzymes Dependent on Pyridoxal Phosphate and Other Carbonyl Compounds as Cofactors", eds. by T. Fukui, H. Kagamiyama, K. Soda and H. Wada, Pergamon, 1991, pp. 371—372. に発表.